

Field-induced quasi-periodic coherence effects in certain small magnets.

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Small ferromagnets and anti-ferromagnets with an easy-plane anisotropy have a ground to first excited state (tunnel) splitting which is quasi-periodic in the magnitude of a field applied perpendicular to a principal anisotropy axis. The associated oscillations in thermodynamic quantities might be used to prove the existence of a coherent ground state even when the tunnel splitting itself cannot be directly detected.

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The study of small magnets tests our understanding of the transition between quantum and classical physics. In the classical regime the order parameter, i.e., the magnetization, of a ferromagnet points in one of a number of equivalent directions which correspond to a minimum of the macroscopic anisotropy energy. On the other hand in the quantum world of small magnets the ground state comprises a coherent superposition of all of these equivalent equilibrium directions. While there is now fairly strong evidence [1] of *relaxation* via quantum *tunneling* in Mn_{12} the observation of a *coherent ground state* remains an elusive goal. The only experimental evidence, for the anti-ferromagnet ferritin [2], remains highly controversial.

The principal purpose of this Letter is to show, for small ferromagnets and anti-ferromagnets with an *easy-plane* anisotropy, there exist rather dramatic level crossing effects. Unlike similar easy-axis magnets which have tunneling effects very sharply peaked at level crossings, the tunnel splitting *oscillates* as a function of the magnet field. The period, e.g., $\Delta H = 2H_{\parallel}$ for a ferromagnet, is determined by an easy-to-measure bulk anisotropy field H_{\parallel} . The observation of this oscillatory signature can provide an unrefutable proof of coherence, and since $M = -\partial F/\partial H$ where F is the free energy, there is necessarily an oscillatory component in the magnetization, and other thermodynamic quantities, which might be readily detected even if the splitting cannot.

The ferromagnet is modeled by a single large spin subject to the external and anisotropy fields [5], i.e., the Hamiltonian $\mathcal{H} = g\mu_B \vec{S} \cdot \vec{H} + K_{\parallel} S_z^2 + K_{\perp} S_x^2$ where without loss of generality it is assumed that $|K_{\parallel}| > |K_{\perp}|$. For an easy plane magnet $K_{\parallel} > 0$. The energy parameters K_{\parallel} , K_{\perp} and, for the anti-ferromagnet, J all scale as S^{-1} . The equivalent physical quantities are $H_{\parallel} = K_{\parallel}/S$, $H_{\perp} = K_{\perp}/S$ and $H_e = J/S$. This is important in ratios such as $(h/K_{\parallel}) = (Sh/H_{\parallel})$.

The problem is formulated [3,4] in terms of auxiliary particles. Consider a ferromagnet. A basis $|S_z\rangle \equiv |n\rangle$ is chosen. Then an auxiliary particle, a fermion f_n , is associated with each state via the mapping $|n\rangle \rightarrow |f_n^{\dagger}\rangle$ where $|\rangle$ is a non-physical vacuum without any auxiliary

particles. Defined is a bi-quadratic version of an operator \hat{O} via: $\hat{O} \rightarrow \sum_{n,n'} f_n^{\dagger} < n | \hat{O} | n' \rangle f_{n'}$. The constraint $Q = \sum_n \hat{n}_n = \sum_n f_n^{\dagger} f_n = 1$. It has been shown [3] that such schemes preserve all operator multiplication rules including commutation rules. The replacement rule is applied to the Hamiltonian \mathcal{H} to yield, taking $g\mu_B \vec{H} = -h\hat{z}$:

$$\mathcal{H} = \sum_n \left(K_{\parallel} n^2 - nh + \frac{1}{4} K_{\perp} [(M_n^{n+1})^2 + (M_n^{n-1})^2] f_n^{\dagger} f_n + \frac{1}{4} K_{\perp} \sum_n M_n^{n+1} M_{n+1}^{n+2} (f_{n+2}^{\dagger} f_n + H.c.) \right), \quad (1)$$

where the $M_n^{n+1} = [S(S+1) - n(n+1)]^{1/2}$ are the matrix elements of S^{\pm} . This is *two* tight binding models of spinless fermions f_n^{\dagger} . The constraint $Q = 1$ implies this is a single particle problem.

The two “chain” structure reflects the fact that the “hopping” term in Eqn. (1) couples “sites” with indices which differ by two. This structure implies immediately a spin-parity effect found by Loss et al. [6], and von Delft and Henley [7]. For the case of integer spin, Fig. 1, the two chains comprise the sites $n = -S, -(S-2), -(S-3) \dots (S-3), (S-2), S$ and $n = -(S-1), -(S-3), -(S-5), \dots (S-5), (S-3), (S-1)$ which are both symmetric relative to $n = 0$. On the other hand for half-integer spin, Fig. 2, the chains are $n = -S, -(S-2), -(S-3) \dots (S-5), (S-3), (S-1)$ and $n = -(S-1), -(S-3), -(S-5), \dots (S-3), (S-2), S$, which are equivalent to each other through the map $n \rightarrow -n$ but which lack the symmetry about $n = 0$. Because of the equivalence of the two chains there must always be a double (Kramers’) degenerate ground state, without a tunnel splitting, for half-integer spin, while because of symmetry about $n = 0$, there can be tunnel split pairs for integer spin.

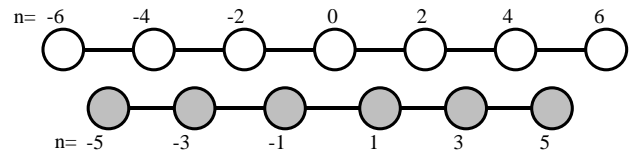


FIG. 1. The two chains for integer spin each have symmetry about $n = 0$

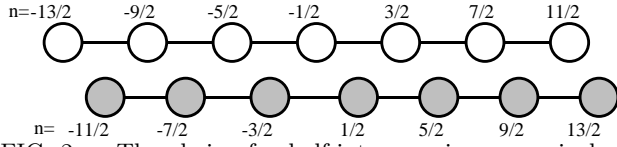


FIG. 2. The chains for half-integer spin are equivalent though the map $n \leftrightarrow -n$

There is a key *fixed point* [8] when $K_{\perp} \rightarrow 0$. All off-diagonal matrix elements are zero, the diagonal energies are $K_{\parallel}n^2 - hn$, and for an *integer spin easy-plane ferromagnet*, i.e., with $K_{\parallel} > 0$, and in zero field ($h = 0$), the ground state lies on the site $n = 0$, and therefore the even site chain. The first excited states at an energy K_{\parallel} are located on the sites $n = \pm 1$ and corresponding to the odd site chain. Level crossings occur whenever

$$h = (2n + 1)K_{\parallel}; \quad n = 0, 1, 2, 3, \dots, \quad (2)$$

which has the period $2K_{\parallel}$. With this period the splitting between the ground state and the first excited state undergoes sawtooth oscillations with amplitude $\sim K_{\parallel}$ and with each level crossing the ground state passes from one chain to the other. Given that as a function of K_{\perp} there are no singularities in the characteristic determinant, this fixed point will govern the behavior for all values of this parameter. That this is the case for a ferromagnet is verified by both the analytic and numerical calculations described below.

The vicinity of the fixed point with

$$S^2 K_{\perp} < K_{\parallel} \quad (3)$$

defines the *small particle limit*. The corrections to the ground state $|n = 0\rangle$ are perturbative, however the excited states split. These are $(1/\sqrt{2})[|1\rangle \pm |-1\rangle]$ with energies $K_{\parallel} \pm K_{\perp}$. The smallest $h = 0$ splitting $K_{\parallel} - |K_{\perp}|$ determines the amplitude of the near saw-tooth oscillations. This splitting has nothing to do with tunneling. However the ground state is clearly “coherent” in the sense $\langle \vec{S} \rangle = 0$, i.e., the order parameter is not localized in a particular direction in the $x - y$ -plane. And if, e.g., the initial state is $(1/\sqrt{3})[|0\rangle + |1\rangle + |-1\rangle]$, $\langle \vec{S} \rangle$ has a magnitude of $\sim S$ and points in the positive x -direction. With a frequency $\omega_1 = H_{\parallel}$, it oscillates rapidly between the $+x$ and $-x$ -directions. While with the frequency $\omega_2 = H_{\perp}$ these oscillations precess in the perpendicular plane so that one quarter of a long period later the rapid oscillations are between the $\pm y$ -directions. Such oscillatory behavior is characteristic of coherence.

Quite generally Schrödinger’s equation

$$\begin{aligned} & (\epsilon - (K_{\parallel}n^2 - nh))a_n \\ &= \frac{1}{4}K_{\perp}M_{n+1}^{n+1}M_{n+1}^{n+2}[(a_{n+2} - a_n) + (a_{n-2} - a_n)], \end{aligned} \quad (4)$$

involves finite differences, where the wave-function $\Psi = \sum_n (-)^n a_n f_n^{\dagger} | \rangle$. When the inequality (3) is reversed the particle is *large* and a continuum approximation to this Schrödinger’s equation is appropriate.

Within the definition of a Fourier transform, $a_n = (1/\sqrt{2\pi}) \int_{-\infty}^{\infty} dp f(p) e^{-ip(n-d)}$, the function $f(p)$ is defined for the even site chain and $h = 0$. For finite h the center of the real space potential is displaced by $d = h/2K_{\parallel}$ and the odd site chain is accommodated via a $d = 1 + (h/2K_{\parallel})$. Assuming $K_{\perp} < 0$, the continuum approximation to Eqn. (4) is:

$$\left(\epsilon - \frac{h^2}{4K_{\parallel}} + K_{\parallel} \frac{\partial^2}{\partial p^2}\right) f(p) = -\frac{S^2 K_{\perp}}{2} [\cos 2p - 1] f(p), \quad (5)$$

which is Mathieu’s equation [9]. The potential is periodic with period $\Delta p = \pi$ and the low lying solutions form bands. For a given energy, a solution might be characterized by a wave-vector k and Floquet’s (Bloch’s) theorem [9] implies that solutions are of the form $f_k(p) = e^{ikp} u_k(p)$ where $u_k(p) = u_k(p + \pi)$. That a_n be finite implies $k = d$ (to within trivial translations). Within a given well of the periodic potential, the low lying states have wave-functions which to a good approximation are those of a harmonic oscillator. Taking $K_{\perp} < 0$, around $p = 0$, $f(p) = (1/\sqrt{\beta\sqrt{\pi}}) e^{-p^2/2\beta^2}$ with $\beta^2 = S\sqrt{K_{\parallel}/K_{\perp}}$, and the nominal ground state energy is $(h^2/4K_{\parallel}) + (\omega_0/2)$; $\omega_0 = 2S\sqrt{K_{\parallel}K_{\perp}}$. Because of tunneling between wells this ground state level becomes a band, i.e., the energies $\epsilon_k = (h^2/4K_{\parallel}) + (\omega_0/2) + (w/2) \cos \pi k$ where the width [9] $w = 8\sqrt{2/\pi}\omega_0 S_f^{1/2} e^{-S_f}$ and where the action $S_f = 2S\sqrt{(K_{\perp}/K_{\parallel})}$.

The result for the “tunnel splitting”, i.e., the difference in energy between the ground states for the even and odd chains is

$$\begin{aligned} \delta E &= 4\sqrt{\frac{2}{\pi}} \omega_0 S_f^{1/2} e^{-S_f} \cos(\pi \frac{Sh}{2H_{\parallel}}); \\ S_f &= 2S\sqrt{(H_{\perp}/H_{\parallel})}. \end{aligned} \quad (6)$$

The numerical work shown in Fig. 3 confirms this result

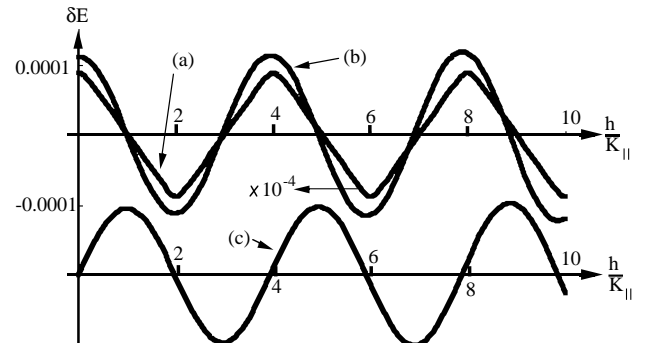


FIG. 3. Each plot corresponds to $K_{\parallel} = 1$. For (a) $K_{\perp} = .0003$, $S = 40$, and the saw-tooth tunnel splitting $\sim K_{\parallel}$ has been divided by 10^4 . Both (b), with integer spin $S = 40$, and (c), with the half-integer value $S = 81/2$, have $K_{\perp} = .03$ and the form is sinusoidal. Notice the $\pi/2$ phase shift.

that large particles have a tunnel splitting which oscillates as $\cos(S\pi h/2H_{\parallel})$. This with the equivalents for an anti-ferromagnet, are the principal results of this Letter.

A perpendicular magnetic field, i.e., one lying in the $x-y$ -plane, couples the two chains. Still, for a larger particle and $K_{\perp} < 0$, the wave-function, a_n , is extended, does not alternate in sign between sites, and is well localized near the center of a chain. The operators S^{\pm} , to a good approximation, cause translations by one lattice site, i.e., they convert the ground state on one chain into that on the other. The matrix elements of $h_x S_x = (h_x/2)[S^+ + S^-]$ are approximately $h_x S/2$ while those of $h_y S_y$ are negligible. Assuming that h is smaller than the splitting $\sim \omega_0$ between the the ground doublet and other excited states, the splitting of the doublet is:

$$\delta E_h = \sqrt{(\delta E)^2 + (S h_x)^2}. \quad (7)$$

Evidently, the field scale it determined by the tunnel splitting $\delta E/S$ and implies a rather careful alignment is required in order to observe oscillations. If $K_{\perp} > 0$, a_n alternates in sign between sites and the role of the x and y axes are interchanged.

Again for a large particle (and $K_{\perp} < 0$), since S_x has large, and S_y very small, matrix elements within the low lying doublet, it follows that if the initial condition puts the system in an approximately equally weighted linear combination of these two states, the magnetization will oscillate in the x -direction at a frequency corresponding to the tunnel splitting, *but* the component in the y -direction is negligible. Thus, in passing from a small to a large particle the magnetization becomes localized in the x -direction. Again for $K_{\perp} > 0$ the role of the x and y axes are interchanged.

Turning to spin-parity effects, consider a *small particle with half-integer spin*. The fixed point now has level crossings occurring whenever $h = 2nK_{\parallel}$ $n = 0, 1, 2, 3 \dots$ which reflects a shift of $\pi/2$ relative to the integer spin case. Kramers' degeneracy corresponds to the level crossing at $h = 0$, but apart from the $\pi/2$ phase shift a half integer small particle behaves like its integer spin equivalent.

Similarly for a *large particle and half-integer spin*, all is the same as for the integer spin case except for the $\pi/2$ phase shift. In particular in the tunnel splitting, Eqn. (6), the cosine is replaced by a sine.

An *easy-axis* ferromagnet [5] is quite different from its *easy-plane* equivalent. In particular there is no oscillatory field dependence.

For larger fields an *easy-plane* anti-ferromagnet is much like a similar ferromagnet and there is again a quasi-periodic modulation of the tunnel splitting. The effective Hamiltonian [10] $\mathcal{H} = g\mu_B \vec{S} \cdot \vec{H} + J\vec{S}_A \cdot \vec{S}_B + K_{\parallel} [(S_{A,z})^2 + (S_{B,z})^2]$ contains the external field, exchange and a suitable anisotropy energy. The exchange field J couples the sub-lattices "A" and "B" and it is

assumed that $S_A = S_B = S$ unless stated otherwise. The auxiliary particles $a_{n,m}$ create single particle states $|n, m\rangle \equiv |a_{n,m}^{\dagger}\rangle$ which map to the $|S_z^A = n + m, S_z^B = -n\rangle$. The constraint is $Q_m = \sum_n a_{n,m}^{\dagger} a_{n,m} = 1$, and the auxiliary particle Hamiltonian [4],

$$\mathcal{H}_m = \sum_n \left[\epsilon_n a_{n,m}^{\dagger} a_{n,m} + t_n^{n+1} (a_{n+1,m}^{\dagger} a_{n,m} + H.c.) \right] \quad (8)$$

where, the diagonal energies are $\epsilon_n = -J(n+m)n - K_{\parallel}[(n+m)^2 + n^2]$, and the hopping matrix elements $t_n^{n+1} = (J/2)M_{n+m}^{n+m+1}M_n^{n+1}$. Hopping couples *neighboring* sites, and there is a distinct chain for every value of the quantum number $m \equiv S_z$.

The *chains* are roughly equivalent to the *sites* for the ferromagnet. The chains with m values which differ by 2 are coupled by the inter-chain hopping terms which arises when the term $K_{\perp}[S_{A,x}^2 + S_{B,x}^2]$ is added. The structure comprises two distinct two dimensional networks, the equivalent of the chains for a ferromagnet, and as the magnetic field changes the ground state can pass from one network to the other causing the tunnel splitting to oscillate in a quasi-periodic manner. Here it is *not* assumed that $K_{\perp} < K_{\parallel}$. The larger and smaller of the two will be denoted K and k respectively.

The period of the oscillations is determined by the condition for level crossings. The details are different for small and large particles. A *small particle* is defined by

$$J > S^2 K_{\parallel} \quad (9)$$

For a given chain, with index $m (\equiv S_z)$, the exchange energy $J\vec{S}_A \cdot \vec{S}_B$ dominates the anisotropy energy K_{\parallel} and trivially the ground state has an energy [4] $(J/2)|m|(|m|+1) - mh$. The fixed point level crossings occur when

$$h = J(n+1); \quad n = 1, 2, 3 \dots, \quad (10)$$

i.e., the first *possible* crossing, and a zero of the tunnel splitting, occurs when $h = 2J$ and otherwise has period $\Delta h = J$. Notice there is a phase shift of $\pi/2$ relative to level crossings for a similar ferromagnet, Eqn(2), and that $J/2$ has replaced the anisotropy parameter K_{\parallel} . The magnitude of the tunnel splitting depends upon another small to large cross-over. If $S^2 K_{\perp} < J$ the particle is *twice times small* and the periodic saw-tooth like splitting is $\sim J = H_e/S$. Here the anisotropy energy is irrelevant and similar periodic behavior will occur for a twice small *easy axis* anti-ferromagnet.

When this latter inequality is reversed the particle is *small-large* and it is implied that $K_{\perp} = K = H_a/S$, $K_{\parallel} = k$. There are two regimes. For the *small field regime*, $h < \omega_0 = 2S\sqrt{KJ} = 2\sqrt{H_a H_e}$, the axis of quantization is rotated to lie along the x -direction, which interchanges the role of, $K_{\perp} = k$ ($= 0$ for simplicity) and $K_{\parallel} = K$ and the field term is hS_x . As a result, the

inverse of inequality (9) is satisfied, the wave-functions on the chains are those of an harmonic oscillator, and the chain ground state energies are [11] $(\omega_0/2) + Jm^2/2$. The *very small field* limit applies when $h < J = H_e/S$ whence the coupling between the chains is a perturbation. The field couples each chain m to the *first excited state* on two adjacent chains $m \pm 1$, with a matrix element $h\beta/2\sqrt{2}$, $\beta^2 = 2S\sqrt{K/J}$. The diagonal energy correction is $-2(h\beta/2\sqrt{2})^2/\omega_0$. An off-diagonal term $t_h = -(h\beta/2\sqrt{2})^2/\omega_0$ couples the $m = \pm 1$ chains via an excited state on the $m = 0$ chain. This splits the pair, with the lower energy being $(J/2) - 3(h\beta)^2/8\omega_0$. For very small fields the splitting is therefore

$$\delta E = \frac{J}{2} - \frac{(h\beta)^2}{8\omega_0} = \frac{J}{2} - \frac{1}{8} \frac{h^2}{J} = \frac{SH_e}{2} - \frac{1}{8} \frac{Sh^2}{H_e}. \quad (11)$$

For *larger fields*, but still in the small field regime, the off-diagonal coupling t_h exceeds the difference in energy between adjacent sites and a continuum approximation is appropriate. The problem reduces [12] to that for a ferromagnet and the result is Eqn. (6) with $h = 0$, $H_{\parallel} \rightarrow H_e/2$ and $H_{\perp} \rightarrow -h^2/2H_e$. The zero point energy for motion perpendicular to the chains is $\sim h$ while that associated with motion along the chains is ω_0 . The equality of these two energies indicates the point at which the appropriate axis of quantization changes and implies the small to large field inequality quoted above.

In the large field regime, $h > \omega_0$, reverting to an axis of quantization defined by the field direction, the ground state energy for the chain labeled m is again $(J/2)|m|(|m| + 1) - mh = (J/2)[m - (h/J) + (1/2)]^2 - (h^2/2J) - (J/8)$ and represents an harmonic potential, centered at $(h/J) - (1/2)$, for the motion perpendicular to the chains. The coupling between chains is $S^2K_{\perp}/2$ and Eqn. (6) again applies with $H_{\parallel} \rightarrow H_e/2$, $H_{\perp} \rightarrow 2H_{\perp}$, and with the cosine replaced by a sine [12]. The same result is valid for small *integer* values of $j = |S_A - S_B|$ the excess, or net, spin. For small *half-integer* j values after the substitution $H_{\parallel} \rightarrow H_e/2$, Eqn. (6) is valid, as written.

For a *larger magnet* when inequality (9) is reversed, the chain ground state energy is again $(\omega_0/2) + (1/2)m^2J - mh$, identical, apart from a constant, to the site energy for the ferromagnetic problem with the replacement $K_{\parallel} \rightarrow J/2$. The level crossings correspond to $h = J(2n + 1)/2$, i.e., have period J . Also as for the previous cases, the magnitude of the tunnel splitting depends upon another small to large cross-over. Now if $S^2K_{\perp} < J$ the particle is *large-small* and the periodic splitting $\sim J = H_e/S$. When this inequality is reversed, corresponding to the *large-large* case, after the substitutions $H_{\parallel} \rightarrow H_e/2$ and $H_{\perp} \rightarrow 2H_{\perp}$, the result is Eqn. (6) for integer j while the cosine is replaced by a sine for half-integer j .

Suitable single crystals of molecular magnets would ideal for studying the predictions made here. The only

relevant experimental evidence known to the author is for the anti-ferromagnet Fe_{10} [13] and would appear to belong to the small-small limit. The series of small ferromagnets based on Mn, all seem to have an easy axis. However many other systems exist for which the nature of the anisotropy have never been determined.

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